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Nano-crystallization within chemically active glyco-protein hydrogel layers: a possible origin for the long-standing vital effect enigma in the Ca-carbonate skeletons.

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Since the pioneering observations by Bowerbank (1844), optical studies of the Ca-carbonate structures produced by the Invertebrates have long emphasized the taxonomy-linked three-dimensional arrangements of their variously sized and shaped microstructural units (prisms, fibres, foliated structures etc.). In contrast, understanding of the mode of growth of these crystal-like units began only during recent years, when structural and chemical informations collected using new instruments such as atomic force microscopes and synchrotron radiation based X-ray microscopes led to a complete renewal of our concepts in biocrystallization. Although permanent association of organic components to these mineral structures was long recognized, as well as their overall glycoprotein composition (Schlossenberger, 1856), improvements of biochemical characterizations occurred during the 60's only. In parallel, evidence rapidly grew that crystallization of these Ca-carbonates was submitted to suprizing "vital effects" (Urey, 1951). Not only is the overall mineralogy of the skeletons fully controlled by the organisms (with sometimes aragonite and calcite simultaneously produced), but within the crystal-like units, at the minor element concentration and isotopic fractionation levels, species-specific and micro-structure dependant behaviours were made obvious. In parallel to a bottom-up approach dealing with in vitro interactions between organic compounds and newly formed minerals in saturated solutions, a reverse approach was followed through improvement of microstructural analysis of the Ca-carbonate skeleton units. This investigation, mostly carried out on the major groups involved in environmental studies, has shown that the basic biomineralization unit is an isochronic growth-layer, the thickness of which is in the micrometer

range. Worth noticing here that this micrometer-thick crystallization layer is also the elemental environment recording unit. Additionally, synchrotron-radiation based fluorescence maps have shown that the organic compounds distributed throughout the skeleton units exhibit indications of a cyclicity in the secretory process corresponding exactly to the banding pattern that can be made visible through etching processes. As a result, interfingering of mineral and organic phases clearly occurs at a submicrometric level. AFM phase images bring support to this hypothesis. In every structures studied to-date, a strong contrast is observed between round-shaped units of few tenths of nanometers in length and the interactive coating of these nodules. We hypothesise that this highly interactive component surrounding the nanograins represents the organic phase distributed within the skeleton growth units (as shown by X-ray fluorescence mapping), or more precisely, the remains of the organic phase entrapped within the growth layer after the crystallization process. TEM data recently presented by A. Baronnet and col. (Nancy SFMC meeting, Jul. 2006) show that the mineral phase consists of nanometer-sized crystals, that are the actual mineral units. Thus these nanometer sized crystals were formed within the chemically active environments of the micro-thick growth layers, in which polymerized glucids, proteins and water were associated in various proportions and taxonomy-linked compositions. Environmental factors (e.g. temperature) may directly influence the reactivity of these complex blends of organic molecules, resulting in the microstructural specificity of the vital effects.

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